of nonzero $n$'s in $\mathfrak{N}$. Equation (A10) is a direct consequence of rule 3.

Examples:

$$\sum_{i=1}^{N} S_i^z S_{i+1}^z(310) = \tfrac{1}{4}[6-(4\times 2)](310) = -\tfrac{1}{2}(310),$$

$$\sum_{i=1}^{N} S_i^z S_{i+1}^z(301) = \tfrac{1}{4}[6-(4\times 2)+4](301) = \tfrac{1}{2}(301).$$

The chain of largest number of spins that we can treat using this numerical method depends on the maximum number of digits that a particular computer can handle. On the other hand, the application of the method is limited by the fact that none of the $n$'s can have a value larger than 9. Since the matrix elements with respect to states having $z$ component of total spin $S_z=M$ or $S_z=-M$ are identical, we have to deal only with half the total matrix, i.e., with values $m=\frac{1}{2}N$, $r=\frac{1}{2}N$. Therefore, the method is limited to a maximum of 18 spins in the chain, which is a larger number than can be handled by present day computers since 18 spins would require diagonalization of matrices of the order of $4800\times 4800$.

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# Direction of Easy Magnetization in Gadolinium

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The direction of easy magnetization in Gd is studied as a function of temperature and pressure. The pertinent experimental results have already been given by Robinson, Milstein, and Jayaraman. A Gd sample was used as the core of a small transformer; a constant input voltage was supplied to this transformer. The secondary voltage was monitored as a function of temperature at several constant pressures. The secondary voltage of the transformer, being proportional to the permeability of the sample, is a sensitive indicator of changes in magnetic structure in the Gd sample. Typically, the secondary voltages behave as follows as the temperature of the transformer is lowered: A sharp rise in the secondary voltage occurs at the Curie temperature, followed by another sharp rise at a temperature well below the Curie point. The magnitude of the secondary voltage at this latter transition is from two to three orders of magnitude greater than at the transition from the paramagnetic to the ferromagnetic state. This transition is interpreted as a magnetic transition in which the direction of easy magnetization in Gd deviates from the $c$ axis. The angle of deviation is discussed in terms of the (small) anisotropy constants resulting from the weak crystalline field in Gd. In terms of the output voltage, one is able to obtain the relative deviations of the direction of easy magnetization from the $c$ axis. The temperatures, as a function of pressure, at which the maximum deviations occur can also be obtained. As the temperature is lowered further, the direction of easy magnetization starts to approach the $c$ axis again. Comparisons are made with other measurements of this angle of deviation.

## INTRODUCTION

IN an earlier paper[1] we presented the results of a study undertaken primarily to determine the dependence of the Curie temperature of gadolinium (Gd) metal upon pressure. Figure 1 is one of the curves that appeared in the earlier paper (it was then numbered Fig. 5). The experimental details are discussed in Ref. 1. Briefly, a Gd sample was used as the core of a small transformer, the secondary voltage, $e_0$, of which was monitored as a function of temperature at several constant pressures. Since the secondary voltage is proportional to the permeability of the sample, it serves as a sensitive indicator of changes in the magnetic structure of the sample. Hence, for example, $e_0$ increases sharply at the Curie point $T_C$ where the sample transforms from the paramagnetic to the ferromagnetic state.

The principal effects observed in Fig. 1 are summarized as follows:

(a) The Curie temperature $T_C$ decreases with increasing pressure as shown by the shift with pressure of the initial increase in secondary voltage. This effect occurs in temperatures ranging from about 250 to 293°K. (Data taken in this temperature range are published as Fig. 3 of Ref. 1.)

* Part of this work was completed when one of us (L.B.R.) held a John Simon Guggenheim Memorial Fellowship.

[1] L. B. Robinson, F. Milstein, and A. Jayaraman, Phys. Rev. 134, A187 (1964).

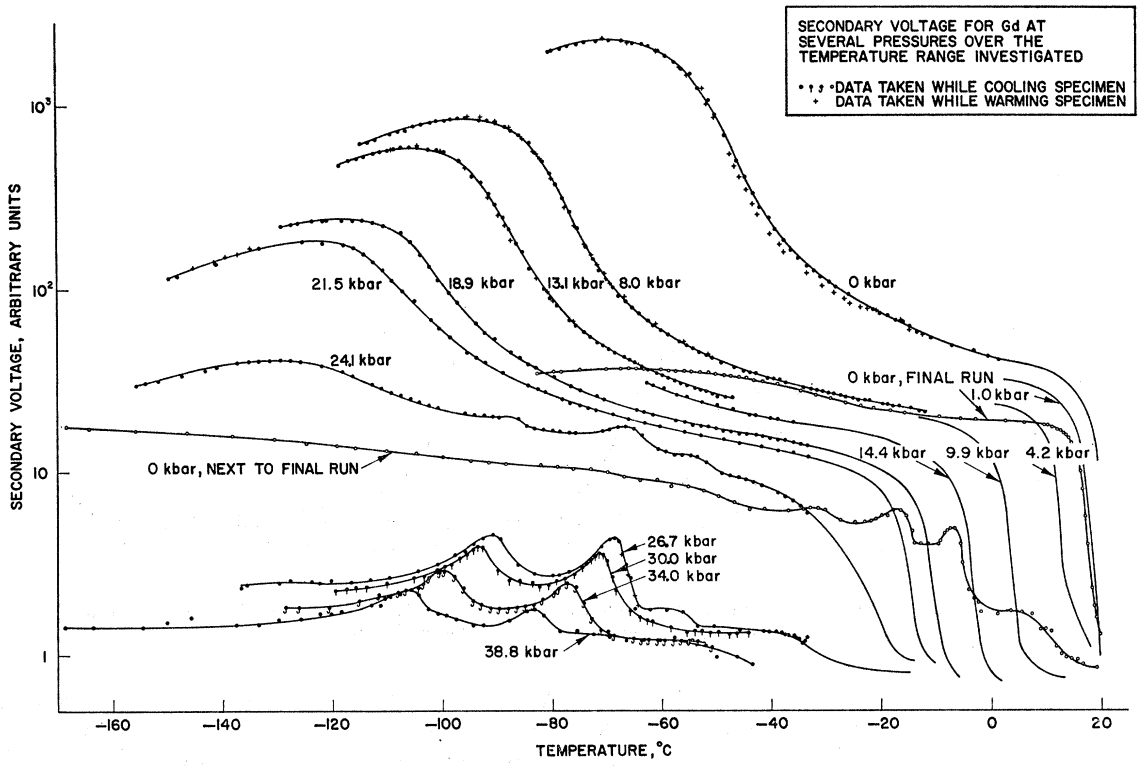


FIG. 1. Relative permeability of polycrystalline Gd specimen as a function of temperature at several pressures.

(b) A change of phase occurs at about 24–26 kbar.[2]

(c) The secondary voltage undergoes a further increase at temperatures well below $T_C$, in the pressure range 0–21.5 kbar. It is seen that these increases of secondary voltage are from one to two orders of magnitude greater than those that occur at the Curie temperature. This effect is shown more clearly in Fig. 2, which displays the secondary voltage on a linear, rather than on a logarithmic scale.

In Ref. 1, the discussion was confined to interpreting effects (a) and (b). The interpretation of effect (c) has not been discussed in detail, and is the subject of the present paper. In particular, it will be shown that, as a result of the unique way in which the magnetocrystalline anisotropy constants of Gd vary with temperature, the curves of Fig. 1 or 2 can be used to determine the pressure and temperature dependence of the easy direction of magnetic ordering.

The Gd ion is in an orbital $S$ state, and therefore the magnetic anisotropy energy of Gd is quite small as compared to the other heavy rare-earth metals, terbium through thulium. It is known, however, from paramagnetic resonance on isolated ions[3] that a small crystalline field potential exists in the form

$$V=B_2^0Y_2^0(\mathbf{S})+B_4^0Y_4^0(\mathbf{S})+B_6^0Y_6^0(\mathbf{S}) +B_6^6[Y_6^6(\mathbf{S})+Y_6^{-6}(\mathbf{S})] \quad (1)$$

through high-order perturbations with the spin-orbit coupling and crystal potential breaking down the Russell-Saunders coupling. Usually $B_2^0>B_4^0>B_6^0$.[4]

This crystalline field potential is equivalent to a magnetic anisotropy energy $E_K$ that is usually expressed in the form

$$E_K=K_0+K_1\sin^2\alpha+K_2\sin^4\alpha+K_3\sin^6\alpha +K_4\sin^6\alpha\cos6\beta, \quad (2)$$

where $\alpha$ is the angle between the magnetization vector and the **c** axis of the crystal, and $\beta$ is the azimuthal angle.

The anisotropy constants $K_1$, $K_2$, $K_3$, and $K_4$ have been measured as a function of temperature by Corner *et al.*[5] ($K_1$, $K_2$, and $K_3$), Graham[6] ($K_1$, $K_2$, and $K_4$), and Darby and Taylor[7] ($K_4$). In both Refs. 5 and 6, $K_1$ is reported to be positive at higher temperatures

[2] This phase change was subsequently determined to be a transition to a samarium-type crystal structure [A. Jayaraman and R. C. Sherwood, Phys. Rev. Letters **12**, 22 (1964)], and similar transitions were subsequently observed to occur in terbium, dysprosion, and holmium [D. B. McWhan and A. L. Stevens, Phys. Rev. **139**, A682 (1965)].

[3] W. Low, Solid State Phys. Suppl. **2**, 113 (1960).

[4] R. J. Elliott, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1965), Vol. IIA, Chap. 7.

[5] W. D. Corner, W. C. Roe, and K. N. R. Taylor, Proc. Phys. Soc. (London) **80**, 927 (1962).

[6] C. D. Graham, Jr., J. Phys. Soc. Japan **17**, 1310 (1962); J. Appl. Phys. **38**, 1375 (1967).

[7] M. I. Darby and K. N. R. Taylor, in *Proceedings of the International Conference on Magnetism, Nottingham, 1964* (The Institute of Physics and the Physical Society, London, 1965), p. 742.

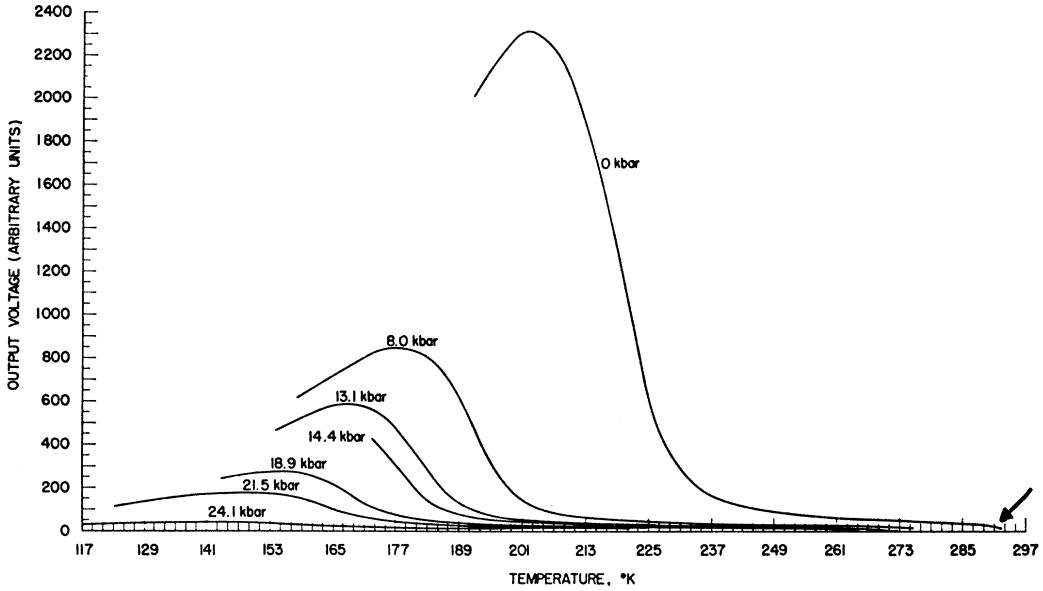


FIG. 2. Anomalous increases in permeability at temperatures well below the Curie point. The Curie point at atmospheric pressure is indicated by an arrow at $T_C$ (0 kbar).

and negative at lower temperatures ($<245$°K,[6] or $<240$°K[5]). $K_2$ and $K_3$ are apparently positive throughout. $K_4$ is less than $K_1$, $K_2$, or $K_3$ by orders of magnitude, so there is little anisotropy energy associated with variations of $\beta$.

Both Corner *et al.* and Graham have determined the easy direction of magnetization of Gd (i.e., the value of $\alpha$, say, $\alpha=\theta$, for which $E_K$ is a minimum, at a given temperature) as a function of temperature, based upon their anisotropy constant measurements. As is seen from Eq. (2), when $K_1$, $K_2$, and $K_3$ are all positive, $E_K$ is a minimum for $\alpha=\theta=0°$. As soon as $K_1$ becomes negative, however, the easy direction $\theta$ departs from 0°.

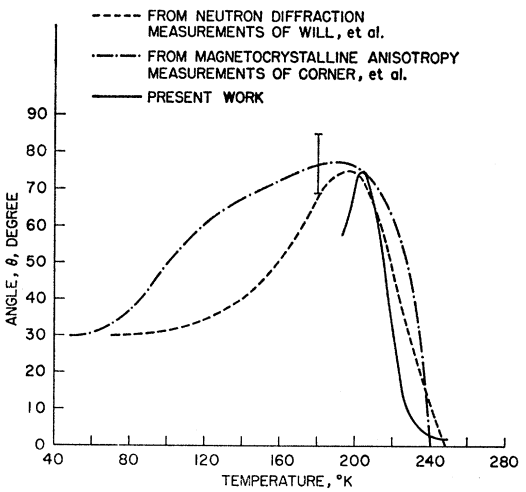


FIG. 3. Easy direction of magnetization of Gd as determined by various experiments. $\theta$ is angle that the easy direction of magnetization makes with the **c** axis.

According to Ref. 5, $\theta$ becomes nonzero at 240°K, increases rapidly to about 77° at 190°K, and with further decreases of temperature the easy direction moves back toward the **c** axis. This is shown in Fig. 3.

Will *et al.*[8] have measured the temperature dependence of $\theta$ by means of neutron diffraction from a Gd single crystal; their results are in good qualitative agreement with those of Corner *et al.*, as is also shown in Fig. 3.[9] Since Will *et al.* were able to determine the relative angle only, they normalized the maximum value of the angle $\theta$ to 75°, to give agreement with the results of Ref. 4. More recently, Cable and Wollan[10] also determined $\theta$ by neutron-diffraction measurements. Their results (not shown in Fig. 3) are in agreement with those discussed above; they observed that $\theta$ departs from the **c** axis at $T=232$°K, which agrees well with the value of this temperature determined in the present work. The results of the present work are discussed below.

## ANALYSIS

Throughout the experiment in which the curves of Fig. 2 were determined, the input voltage and input frequency, the number of primary and of secondary turns, and the configuration of the specimen and the windings were all unchanged. Thus the secondary voltage $e_0$ is proportional to the permeability $\mu$ of the

[8] G. Will, R. Nathans, and H. A. Alperin, J. Appl. Phys. **35**, 1045 (1964).

[9] The dependence upon temperature of the easy direction of magnetization $\theta$ as determined by neutron diffraction agrees more closely in form with that determined from the three anisotropy constants $K_1$, $K_2$, and $K_3$ (Ref. 5) than that based upon the first two constants (Ref. 6).

[10] J. W. Cable and E. O. Wollan, Phys. Rev. **165**, 733 (1968).

Gd specimen, and the variation of $e_0$ depends only upon the variation of $\mu$. The permeability is related to the susceptibility $\chi$ by the relation

$$\mu=1+4\pi\chi. \tag{3}$$

In the ferromagnetic state $4\pi\chi\gg1$, so that $e_0$ is essentially proportional to $\chi$.

In the present experiment, $\chi$ can be taken to be the average value of the change of the component $M_h$ of the magnetization $\mathbf{M}$ in the field direction $\hat{h}$, when the field passes through one half-cycle, from maximum value $\mathbf{H}=H\hat{h}$ to minimum value $\mathbf{H}=-H\hat{h}$, divided by $\Delta H$ $(=2H)$, i.e.,

$$\chi=\langle\Delta M_h\rangle/2H. \tag{4}$$

The average of the value $\Delta M_h$ is taken over random orientations of the crystal axes with respect to the field direction $\hat{h}$, thereby taking into account the polycrystalline nature of the Gd specimen.

In order to determine $\Delta M_h$, it is useful first to consider a given grain or crystallite within the polycrystalline specimen. This crystallite is specified by the orientation of its crystal axes with respect to $\hat{h}$; let the polar angle between $\hat{h}$ and the **c** axis be $\xi$, and the azimuthal angle between $\hat{h}$ and the **a** axis, $\eta$. If, in the absence of an applied field, the orientation of $\mathbf{M}$[11] in the crystallite is determined by minimizing $E_K$, Eq. (2), then in the presence of a field it is specified by minimizing

$$E=E_K-\mathbf{M}\cdot\mathbf{H}, \tag{5}$$

i.e., (for $\mathbf{H}=H\hat{h}$) by the conditions

$$\frac{\partial}{\partial\alpha}[K_1\sin^2\alpha+K_2\sin^4\alpha+K_3\sin^6\alpha+K_4\sin^6\alpha\cos6\beta - HM(\sin\alpha\sin\xi\cos\beta\cos\eta+\sin\alpha\sin\xi\sin\beta\sin\eta +\cos\alpha\cos\xi)]=0 \tag{6}$$

and

$$\frac{\partial}{\partial\beta}[K_4\sin^6\alpha\cos6\beta-HM(\sin\alpha\sin\xi\cos\beta\cos\eta +\sin\alpha\sin\xi\sin\beta\sin\eta)]=0. \tag{7}$$

In the temperature range of interest, $K_1$, $K_2$, and $K_3$[5] are of the order $10^5$–$10^6$ erg cm$^{-3}$, and $K_4$[7]$<10^2$ erg cm$^{-3}$. $H$ in the present experiment is close to 1 Oe, so that $HM$ is about $10^3$ erg cm$^{-3}$. That is, the situation exists in which $K_1$, $K_2$, and/or $K_3$ are about two orders of magnitude greater than $HM$ and $HM$ is at least one order of magnitude greater than $K_4$. Thus Eq. (6) is insensitive to the terms that are multiplied by $HM$, and, upon neglecting these terms, the solution is simply $\alpha=\theta$, the polar angle of $\mathbf{M}$ in the absence of a field. The solution to Eq. (7), upon neglecting the $K_4$ term, is simply $\beta=\eta$.

[11] Throughout this paper, the magnetization vector $\mathbf{M}$ and its magnitude $M$ refer to the localized magnetization, not the net magnetization of the polycrystal.

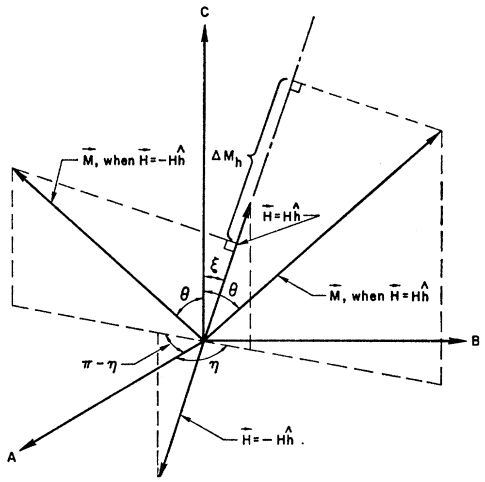


FIG. 4. Vector diagram showing $\Delta M_h$, the change in the component of the magnetization vector $\mathbf{M}$ in the field direction $\hat{h}$, when $\mathbf{H}$ passes from $\mathbf{H}=H\hat{h}$ to $\mathbf{H}=-H\hat{h}$. The vectors $\mathbf{H}$ and the vectors $\mathbf{M}$ all lie in the same plane. The axis labeled $C$ represents the **c** axis in the crystal. $A$ and $B$ are orthogonal axes in the basal plane.

Hence, upon the application of a field of about 1 Oe to the given crystallite, the polar angle $\theta$ between $\mathbf{M}$ and the **c** axis remains unchanged, and the azimuthal angle of $\mathbf{M}$ becomes equal to the azimuthal angle of $\mathbf{H}$ (this is clearly the case for $\mathbf{H}=H\hat{h}$ as well as for $\mathbf{H}=-H\hat{h}$).[12] $\Delta M_h$ is then given by

$$\Delta M_h=M[\cos(\theta-\xi)-\cos(\theta+\xi)], \tag{8}$$

as is seen in Fig. 4, and

$$\langle\Delta M_h\rangle=\int_0^\pi \Delta M_h\sin\xi\,d\xi\Big/\int_0^\pi\sin\xi\,d\xi. \tag{9}$$

Performing the integration, $\langle\Delta M_h\rangle=\frac{1}{2}\pi M\sin\theta$, and from Eq. (4),

$$\chi=(\pi M\sin\theta)/4H. \tag{10}$$

## DISCUSSION

Equation (10) thereby demonstrates that, in the presence of a field $H\approx1$ Oe, the susceptibility (as defined above) of a polycrystalline Gd specimen is approximately proportional to $M\sin\theta$, where $\theta$ is the angle that the direction of easy magnetization makes with the **c** axis (in any one of the grains of the poly-

[12] The existence of domains within a single crystallite is neglected in the above analysis. Since the first three anisotropy constants are several orders of magnitude greater than $K_4$, if domains were to form within a crystallite, they would be expected to form with different values of azimuthal angle, but with $\theta$ remaining unchanged (or changing to $\pi$-$\theta$, an equivalent easy direction). Upon the application of the field $\mathbf{H}$, it is assumed that the azimuthal angle $\beta$ rotates to a position of minimum magnetic energy $-\mathbf{M}\cdot\mathbf{H}$, and thus $\beta$ becomes equal to $\eta$. Under this assumption each crystallite is then, in effect, a single domain, as in the analysis above. It is assumed that there exists no domain wall motion in the magnetization process; this assumption is discussed in the following section.

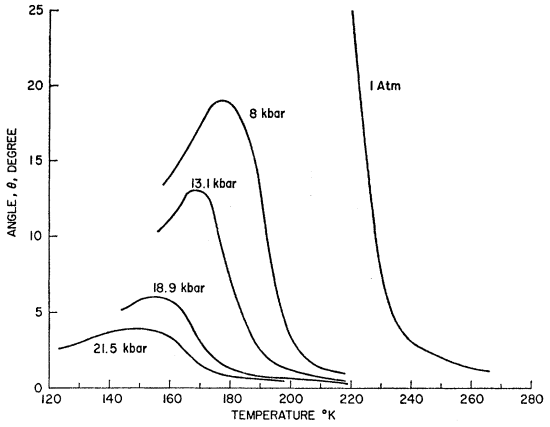


FIG. 5. Dependence of $\theta$ upon pressure and temperature.

crystal). The output voltage of the curves of Fig. 2 can then be written approximately as

$$e_0 = AM \sin\theta. \tag{11}$$

Since it is difficult to determine the constant $A$ exactly from theory, $A$ is chosen so that the maximum value of $\theta$, at atmospheric pressure, is equal to 75°. This is the same maximum value of $\theta$ assumed by Will *et al.* in the interpretation of the neutron-diffraction measurements.

The value of $\theta$, at atmospheric pressure, according to Eq. (11), is compared in Fig. 3 with the results of others, previously mentioned. All three measurements show that the angle $\theta$ rises initially very sharply at about 230–240°K with decreasing temperature. The output voltage result, however, gives some residual deviation from zero at temperatures higher than 240°K. It is thought that $\theta$ does go to zero in the neighborhood of 230–240°K, and that this residual value is an indication of the degree of error present in Eq. (11). The neutron-diffraction experiment shows a sharper drop in the angle, once the maximum is reached, than does the anisotropy constants experiment. The output voltage measurement indicates an even sharper fall-off of the angle with decreasing temperature.

An important assumption made in the analysis of the preceding section is that the effect of domain wall motion could be neglected (i.e., the approximation was made that no domain wall motion takes place). It can be seen that this is indeed a reasonable assumption by considering what the effect of the opposite extreme would be, i.e., what would be the nature of the output voltage curves if complete domain wall movement occurred. In this event, when the field passes through a half-cycle, say, from $\mathbf{H}=-H\hat{h}$ to $\mathbf{H}=H\hat{h}$, the $\pi$-$\theta$ domain would change to a $\theta$ domain by means of domain wall movement. The change of the magnetization component in the field direction would then be given by

$$\Delta M_h = 2M\cos(\theta-\xi), \tag{12}$$

and, for the whole specimen,

$$\langle \Delta M_h \rangle = 2M \int_0^{\pi/2} \cos(\theta-\xi)\sin\xi\, d\xi \Big/ \int_0^{\pi/2} \sin\xi d\xi$$
$$= M[\cos\theta + \tfrac{1}{2}\pi \sin\theta]. \tag{13}$$

The integrals in Eq. (13) pass from 0 to $\frac{1}{2}\pi$ since, in the case of complete domain wall motion, for the applied field in a given direction, say, $\mathbf{H}=H\hat{h}$, there would exist only $\theta$ domains. By contrast, in the absence of domain wall motion, there exist both $\theta$ and $\pi$-$\theta$ domains; hence the integrals in Eq. (9) must pass from 0 to $\pi$.

According to Eq. (13), if domain wall motion were to play an important part in the magnetization process, then the output voltage curves of Fig. 2 would be expected to be approximately proportional to $\cos\theta + \frac{1}{2}\pi\sin\theta$; clearly this is not the case. The $\cos\theta$ term, which would give rise to a large value of $\langle \Delta M_H \rangle$ for $\theta=0°$, is seen to arise as a result of the assumption of domain wall motion. Since the output voltages (Fig. 2) are extremely small for temperatures greater than 240°K ($\theta=0°$), it is concluded that the $\cos\theta$ term is essentially absent from the magnetization process, and that the approximation of no domain wall movement is valid.

Thus, in the analysis leading to Eq. (11), several reasonable approximations have been made regarding the magnetization process of the Gd specimen under the particular experimental conditions that prevailed during the output-voltage measurements. That these approximations are reasonable is corroborated by the fact that good agreement is obtained between the

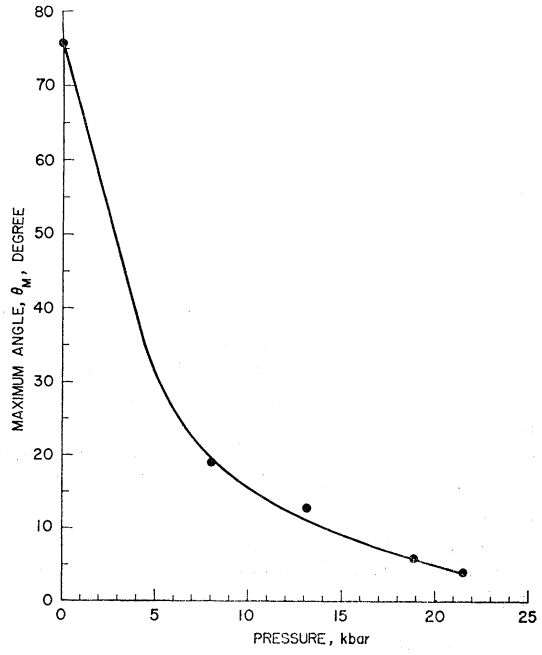


FIG. 6. Maximum deviation of the easy direction of magnetization from the **c** axis, $\theta_m$, in degrees (angular measurement).

present determination of $\theta$, based upon the output-voltage measurements, and the results of neutron-diffraction and anisotropy measurements. This, in turn, allows the previously unexplained anomalies of the output voltage to be correlated with the change of the easy axis of magnetization.

It is of interest to note that Belov and Pedko[13] have observed pronounced peaks in the magnetization of polycrystalline Gd, measured in weak fields, at about 200–240°K. Fields of about 10–100 Oe tended to destroy these peaks, and to result in a magnetization curve closer in form to the Weiss type. Belov has argued that these peaks show the existence of a spiral magnetic structure, similar to that existing in Tb or Dy, which converts to a ferromagnetic structure upon the application of a stronger field.

These peaks are similar in form to what one would expect from the results of the preceding section; i.e., the low-field magnetization measurements of polycrystalline Gd should show peaks in magnetization that are approximately proportional to $\sin\theta$. Thus the present study shows that it is not necessary to assume that Gd possesses a spiral spin structure in order to account for these peaks.

Furthermore, for fields of about 50 oe, or greater, the magnitude of $\mathbf{M}\cdot\mathbf{H}$ is comparable with that of $K_1$, $K_2$, and $K_3$; therefore, fields of this order are strong enough to turn $\mathbf{M}$ away afrom the easy direction $\theta$. When this occurs, the magnetization of the polycrystal will no longer be proportional to $\sin\theta$, but will come closer to the Weiss type of curve. This is in good qualitative agreement with what was observed by Belov and Pedko.

It is also of interest to note that, using techniques similar to those of Ref. 1, output voltage measurements have been made with Gd-Dy alloys[14]; none of the alloys examined exhibited a second increase of output voltage below the Curie temperature. The alloy of minimum Dy content was 16.6% Dy-83.4% Gd; this alloy was ferromagnetic throughout its range of magnetic ordering (the helical spin structure begins to appear at about 50% Dy). Since the anisotropy of Dy is much larger than that of Gd, and since the easy direction of magnetization in Dy is perpendicular to the **c** axis, it is likely that 16.6% Dy was sufficient to cause the spins

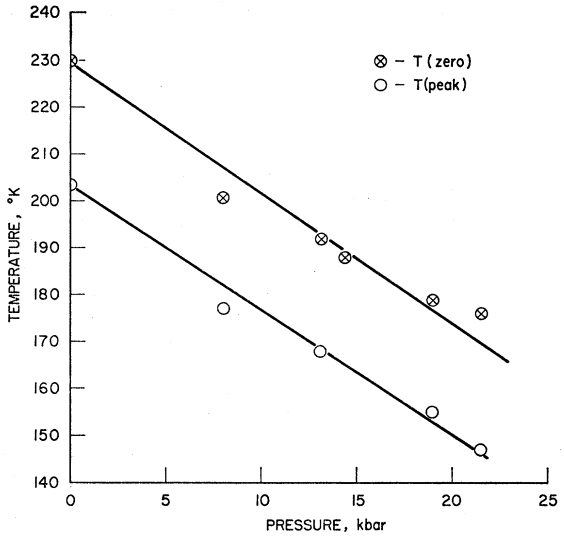


FIG. 7. The variation with pressure of the temperatures at which the easy direction of magnetization departs from the **c** axis, $T$(zero), and at which it reaches its maximum deviation, $T$(peak).

of the alloy to become aligned perpendicular to the $c$ axis. It would be of interest to perform experiments of this sort with alloys of Gd and Dy (or Gd and other rare earths) containing much smaller percentages of Dy.

The effect of pressure upon the angle $\theta$ in Gd, as determined from Eq. (11), is plotted in Fig. 5 (with the exception of the full range of $\theta$ at atmospheric pressure, which is already given in Fig. 3). It is seen that as the pressure increases, and hence interatomic spacing de-decreases, the angle $\theta$ remains small for lower temperatures and does not rise as high as in the lower pressure cases. At 21.5 kbar, the direction of easy magnetization never deviates more than about 4° (angular measurement) from the **c** axis. Figure 6 shows the dependence of the maximum angle $\theta_m$ upon pressure.

Two temperatures of significance appear in Fig. 1, viz., the temperature at which the isobaric curves of Fig. 5 reach a maximum [called $T$(peak)] and the temperature at which $\theta$ extrapolates to zero [called $T$(zero)]. The latter is taken to be the temperature at which the easy direction first deviates from the **c** axis. Both of these temperatures are plotted in Fig. 7 as a function of pressure. It is seen that both change at about the rate $-2.6$°K/kbar, about $1\frac{1}{2}$ times that with which the Curie temperature changes.

[13] K. P. Belov and A. V. Pedko, Zh. Eksperim. i Teor. Fiz. **42**, 87 (1962) [English transl.: Soviet Phys.—JETP **15**, 62 (1962)].
[14] F. Milstein and L. B. Robinson, Phys. Rev. **159**, 466 (1967).